NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Molecular Beam Mass Spectrometry for Analysis of Condensable Gas Components

Tar Analysis Workshop

19th EU Biomass Conference

Berlin

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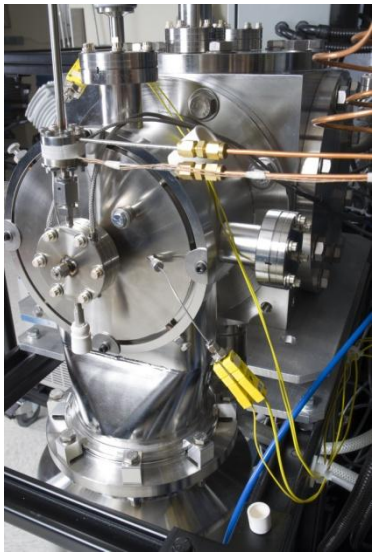
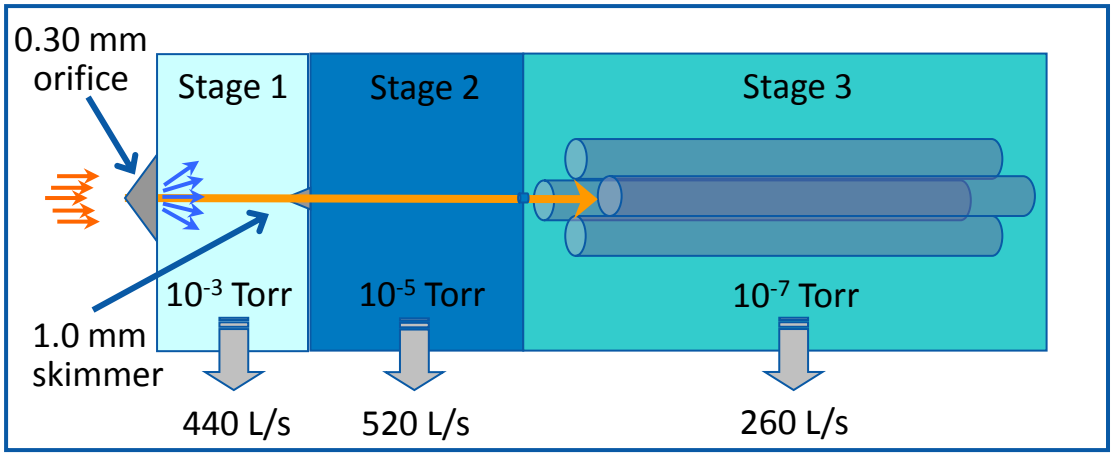
NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Background

MBMS analysis technique developed and used by NREL for >30 years *(originally to study prompt thermochemical phenomena):*



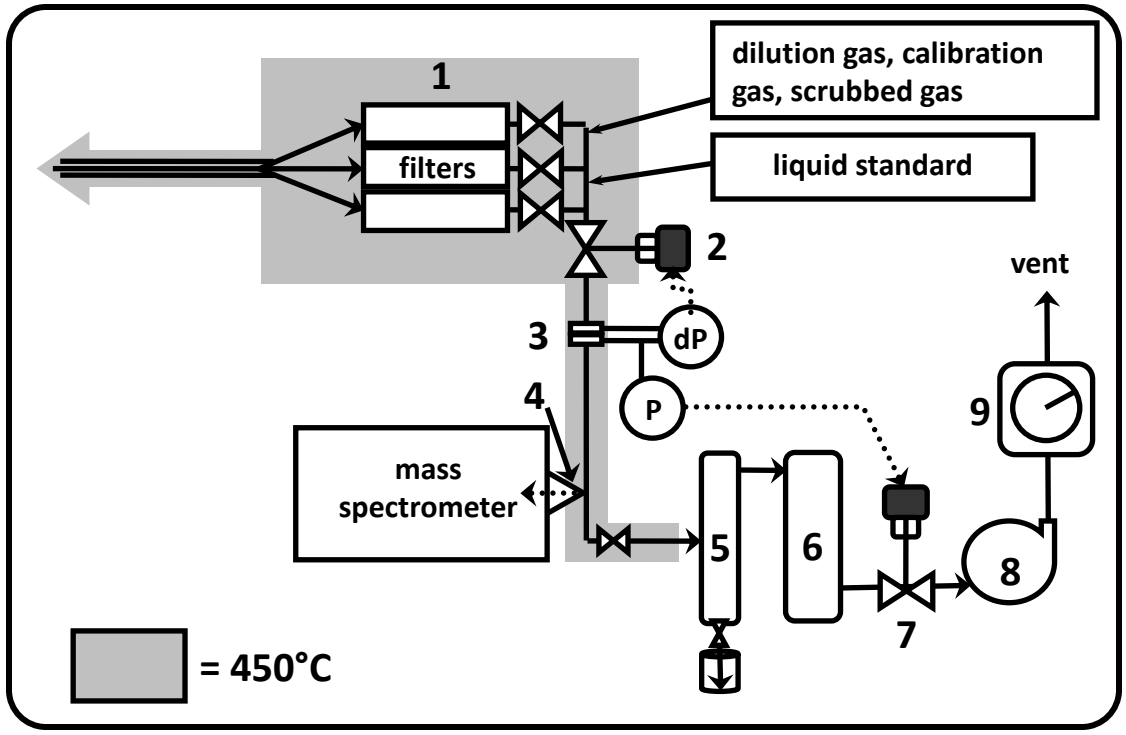
1. Line-of-sight extraction of vapor-phase sample from high T, ambient P environment into mass spectrometer ($P_{source}/P_{Stage1} \geq 10^4$)
2. Supersonic expansion, rapid cooling/rarefaction preserves sample without condensation or reaction
3. Mass analysis provides instantaneous chemical fingerprint of sample
4. Useful for tar and alkali metal vapor analysis



Formation of molecular beam

Transportable instrument for process monitoring

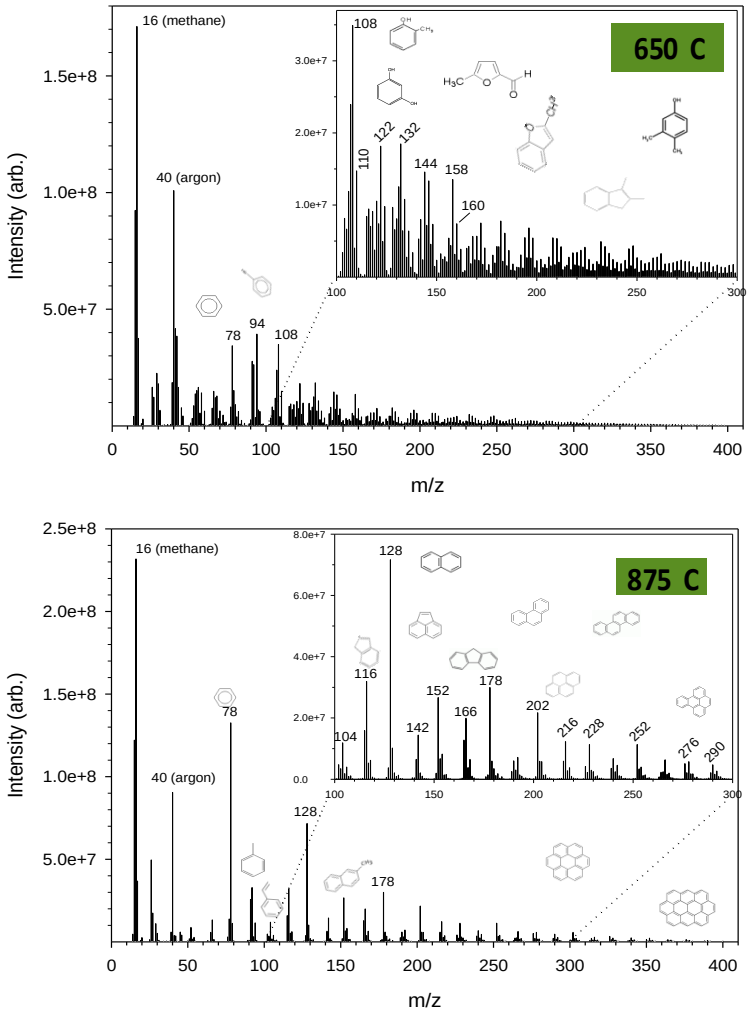
- Constructed field-deployable MBMS (~1995)
- Mass spectrometer cart: ~1 m^2, 300 kg
- On-board, PC-based sample handling and calibration control (temperature, pressure, flow control, gas & liquid standards)



1. Sample manifold
2. Flow control valve
3. Orifice plate flow meter
4. Sampling orifice
5. Condenser
6. Coalescing filter
7. Pressure control valve
8. Sample pump
9. Dry test meter

Results and experience

- Provides real-time, continuous, and robust process monitoring of hot, untreated process gas
- Near-universal detection (typical sensitivity ~1 ppmv)
- Reproducible and stable with routine maintenance
- Learning curve is steep, complex system
- Quantitation is somewhat cumbersome (requires careful injection of liquid standard for *each* species of interest and good measurement of wet volumetric flow)
- Compares well with EU Tar Protocol, but estimations of "gravimetric" tar difficult with limited standard set (injection of heavy tar standards into hot oven problematic due to solvent vaporization and capillary plugging)
- Expensive (approx. $300K U.S.)
- Most valuable during plant startup and initial product gas characterization, less valuable for routine analysis



Mass spectra observed with MBMS during wood gasification at 650° C and 875°C

Current status and future work

- System works, but can be made smaller, lighter, more energy efficient with recent equipment advancements (vacuum pumps, electronics)
- Phase-sensitive detection (molecular beam chopper) could be added to increase sensitivity by >100x
- Commercial MBMS systems are now available (Extrel CMS, Hiden Analytical) that could easily be outfitted for the field

References:

- Evans, R.J., Milne, T.A., "Molecular Characterization of the Pyrolysis of Biomass. 1. Fundamentals" *Energy & Fuels* **1987**, *1* (2), 123-137.
- Carpenter, D.L., Deutch, S.P., French, R.J. "Quantitative Measurement of Biomass Gasifier Tars Using a Molecular-Beam Mass Spectrometer: Comparison with Traditional Impinger Sampling" *Energy & Fuels* **2007**, *21*, 3036-3043.
- Dayton, D.C., French, R.J., Milne, T.A., "Direct Observation of Alkali Vapor Release during Biomass Combustion and Gasification. 1. Application of Molecular Beam/Mass Spectrometry to Switchgrass Combustion" *Energy &Fuels* **1995**, *9* (5), 855-865.
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NREL/National Bioenergy Center: http://www.nrel.gov/biomass

DOE Biomass Program: http://www.eere.energy.gov/biomass

Additional syngas analysis methods under development at NREL

- High-resolution mass spectrometry
- Diode laser spectroscopy
- Laser ablation, REMPI/TOF
- Advanced gas chromatography

High-resolution mass spectrometry

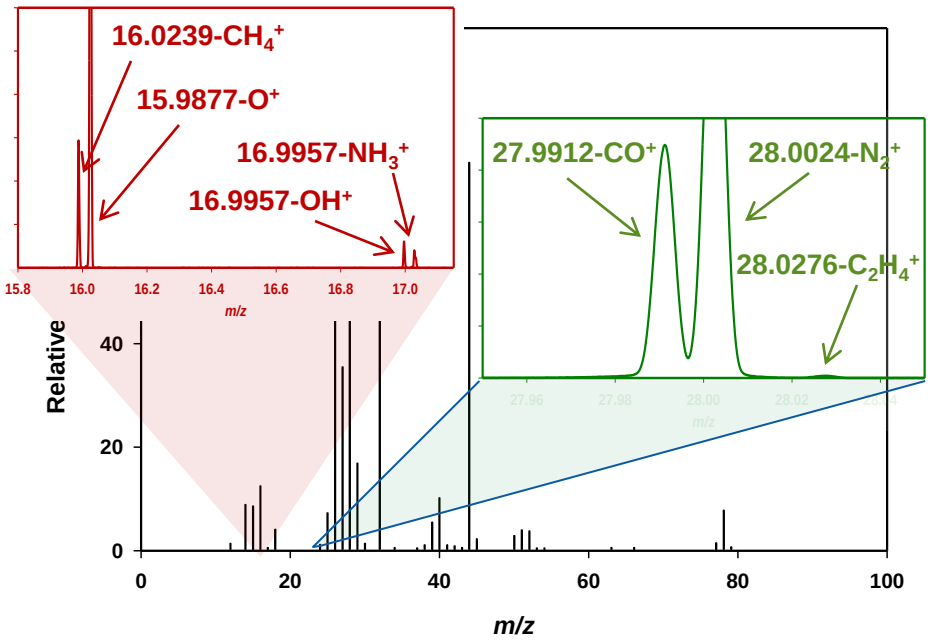
JMS-GCmate II (JEOL Ltd., Japan) high-resolution magnetic sector mass spectrometer installed in TCPDU

- Resolution of 5000 (m/Δm) enables "accurate mass" measurements (elemental compositions)
- Mass range: 1-3000 amu
- Sensitivity: 30 pg/μL (ppt)
- Capable of CI and direct insertion probe operation

Limitations:

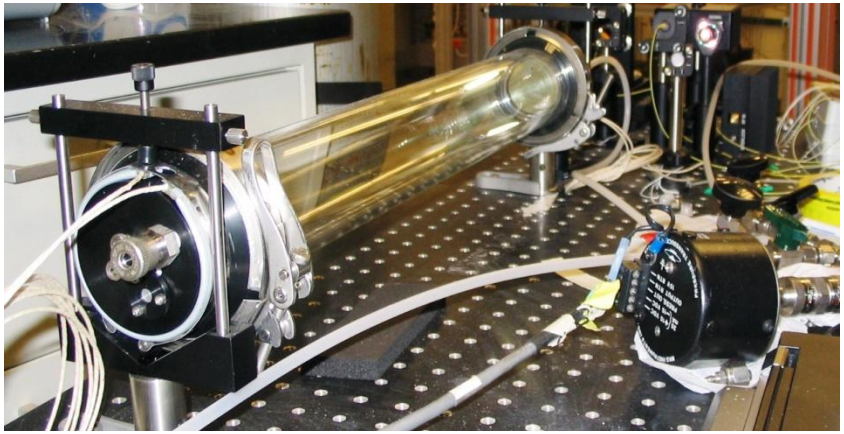
- Capillary inlet may limit throughput of high-mass compounds
- Magnet stability vs. ambient temperature
- Ion source robustness?

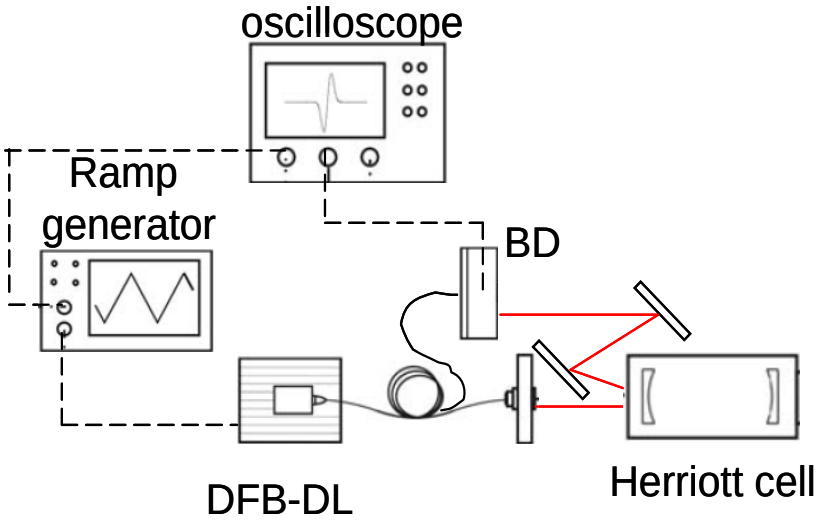
- Motivation: analysis of very low levels of DOE-targeted syngas impurities, e.g. NH_3, HCl, H_2S
- Modified inlet system for continuous monitoring of syngas (still working on heated capillary inlet for tars)
- Can resolve at m/z…
  - 16: $NH_2^+/CH_4^+/O^+$
  - 17: $OH^+/NH_3^+/^{13}CH_4^+$
  - 27: $^{13}C_2H_2^+/HCN^+/C_2H_3^+$
  - 28: $CO^+/N_2^+/C_2H_4^+$



Mass spectrum of scrubbed, wood-derived syngas observed with high-resolution mass spectrometer

Diode laser spectroscopy





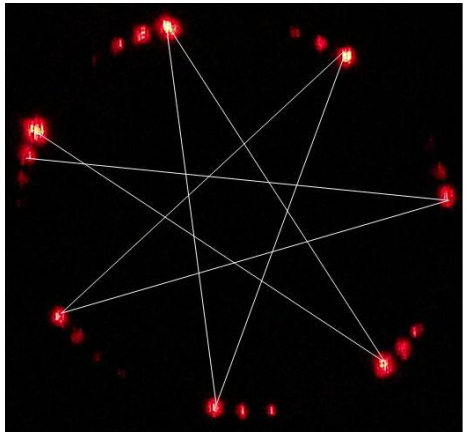
Photograph showing Herriott cell (top) and schematic of diode laser spectrometer. BD – balanced detector, DFB-DL – distributed feedback diode laser

- Based on near-IR absorption spectroscopy
- Detection limit: 0.1 ppmv
- Response time ~ 2 sec
- Expandable to multispecies detection at roughly $5000/component

Limitations:

- Susceptible to absorption interferences, especially water vapor
- High resolution spectroscopy unknown for most species

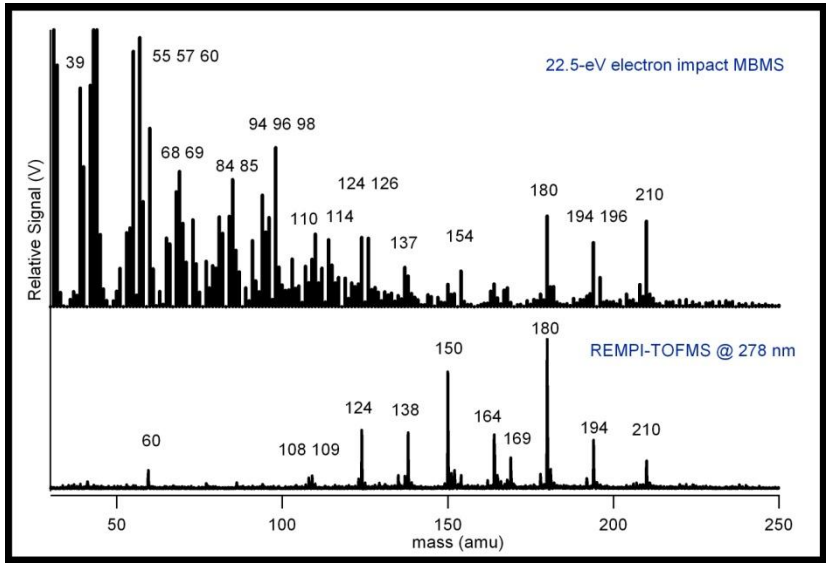
Multipass pattern observed on 2” mirror using 660 nm alignment laser. Effective pathlength ~ 49 meters.

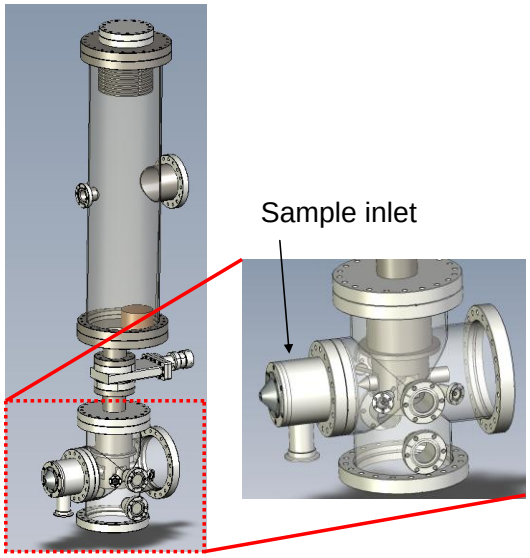


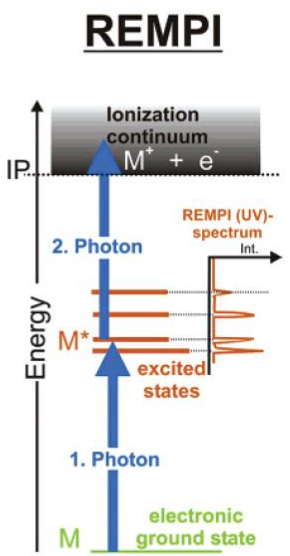
Contact: David Robichaud (david.robichaud@nrel.gov)

Laser ablation, REMPI/TOF

- Laboratory unit for fundamental studies
- Highly selective towards lignin pyrolysis products (see below)
- Screening of catalysts for biomass pyrolysis
- Study effects of mineral salts on pyrolysis of lignin
- Classification of lignin form different biomass feedstocks







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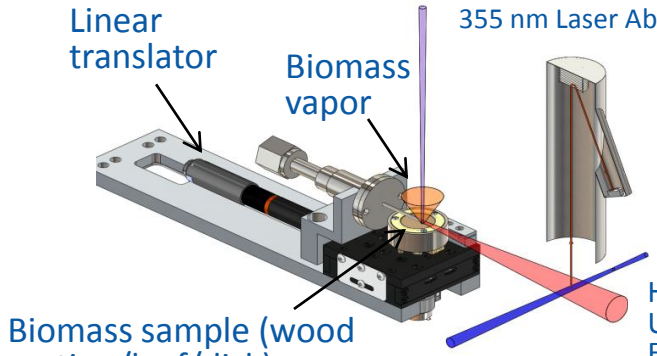

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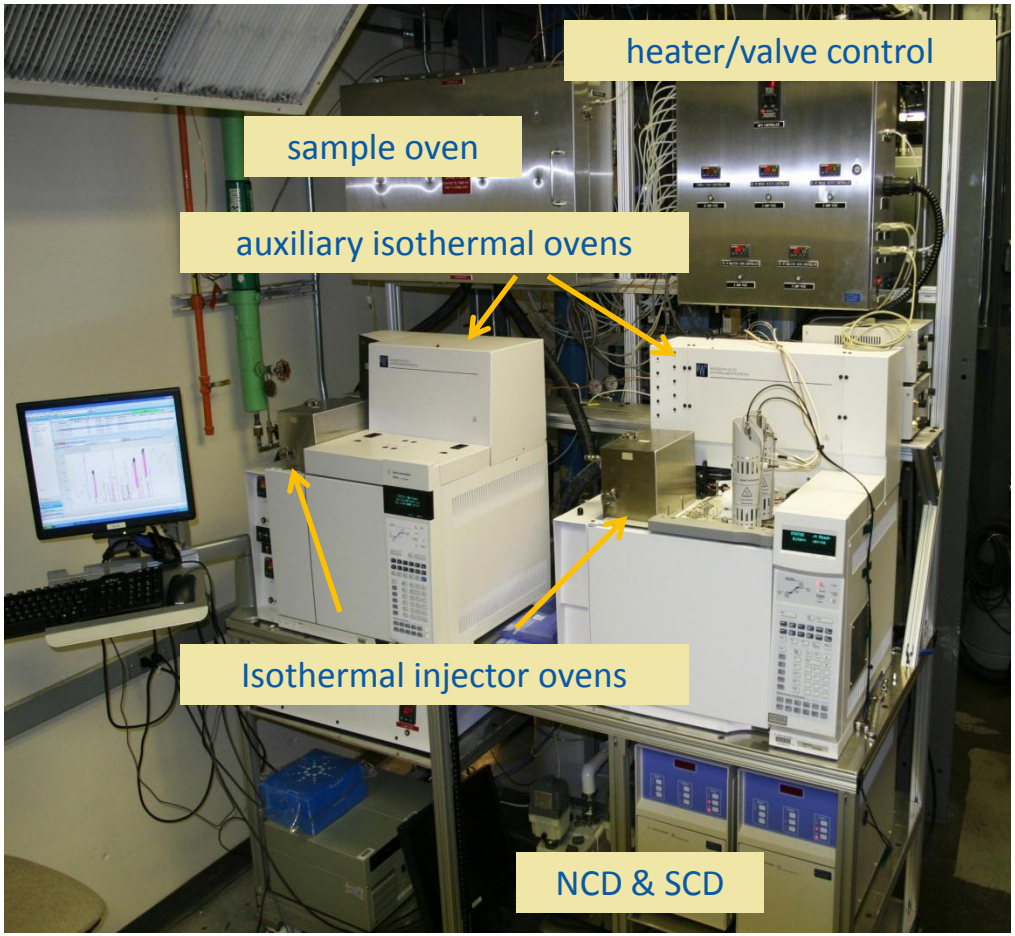
Advanced gas chromatography

- Customized Agilent 6890N & 7890A gas chromatographs
- Accepts heated sample to 325°C
- Dual FID detectors (hydrocarbons through C_{20})
- Dual TCD detectors (permanent gases, tracer gases)
- Nitrogen chemiluminescence detector – NCD (9 N compounds, including NH_3, HCN, pyrrole, pyridine at 0.05 ppmv)
- Sulfur chemiluminescence detector – SCD (16 S compounds, including H_2S, mercaptans, thiophene at 0.1 ppmv)

Limitations:

- Some compounds not detectable at 325°C
- Analysis time – fast analysis: 8 min., detailed analysis: 40 min.



Wasson-ECE Instrumentation (Ft. Collins, CO) customized GC system for analysis of hot syngas up to 325°C.